



Memorandum

To: Kevin Bilash (USEPA) Ref. No.: 11102641.07

From: Daniel W. Smith, PhD./m1, Colleen Costello, David Steele Date: August 24, 2016

cc: Jim Oppenheim (Evergreen), Paul Gotthold (USEPA)

Subject: Remediation Goal for Lead in Sediment

The purpose of this memorandum is to propose a Remediation Goal for lead in sediments of Middle Creek and in the Delaware River at the Marcus Hook Industrial Complex.

1. Background

The Marcus Hook Refinery Operations, A Series of Evergreen Resources Group, LLC (Evergreen) is performing a RCRA Facility Investigation (RFI) within AOI-7 – Former Ethylene Plant at the Marcus Hook Industrial Complex. The RFI is being conducted under a Corrective Action Framework between Evergreen and the U.S. Environmental Protection Agency (USEPA). The scope of the RFI for AOI-7 includes an Ecological Risk Assessment. The key ecological feature of AOI-7 (and adjacent AOI-5 in Pennsylvania) is Middle Creek, a stormwater ditch draining to the Delaware River at the southwestern corner of AOI-7. Middle Creek is tidally influenced along its entire length of 2500 feet. Middle Creek is a roughly trapezoidal, man-made drainage feature with a substrate consisting of 18 to 24 inches of unconsolidated sediment (predominately silt) underlain by variable sized gravel and rip-rap.

The General Chemical Site, and the adjacent Honeywell Site (Solid Waste Management Unit 9) border AOI-7 along its western boundary. The Honeywell Site was originally part of the same industrial complex as the current General Chemical Site, thus they are herein jointly referred to as the General Chemical Site. Middle Creek discharges to the Delaware River within 20 feet of the southern end of this boundary. Former industrial operations at the General Chemical Site include the manufacturing of pesticides. On behalf of Honeywell, Environ International, Inc. (Environ) developed a set of Remediation Goals (RGs) for DDx (4',4'-DDD, 4',4'-DDE and 4',4'-DDT), arsenic and lead (Environ, 2012) in support of the Interim Remedial Measures Work Plan for the Delaware River adjacent to the General Chemical Site. Environ also developed RGs for DDx and arsenic for use in Middle Creek in addition to those developed for the Delaware River. Environ described the methods used as following the methodology submitted to the USEPA on August 15, 2011 and as approved by USEPA on August 19, 2011.

As part of the ongoing AOI 7 Ecological Risk Assessment activities, Evergreen requested that GHD evaluate the RG for lead developed by Environ, and develop an alternate RG if the current RG did not represent current data or site conditions.



2. Target Receptor

In its risk assessment for nearshore sediments in the Delaware River, Environ generated preliminary clean-up levels for lead in sediments based on protection of three receptors: benthos, resident fish, and fish-eating wildlife (osprey and two merganser species) based on the available data at that time. The lowest estimated clean-up level, 150 mg/kg, was for protection of fish. Because of its small home range and consequent high area use factor (100%), the mummichog was the key species mediating risk in the Environ analysis. By comparison, lead sediment RGs for other fish species (i.e., white perch and channel catfish) and other receptors were considerably higher. The RG for white perch and channel catfish were about 4500 mg/kg and 2500 mg/kg, respectively. Specific clean-up levels were not calculated for the fish-eating birds, but estimated bird exposures to lead, via the food chain at 150 mg/kg in sediments, were less than 1/50th of a very conservative No Effects Level for lead. Thus, the lead sediment concentration protective of fish-eating birds would have been much higher than 150 mg/kg. The second most restrictive RG was 570 mg/kg lead, for protection of aquatic benthos, although this estimate did not include potential ameliorative effects of high organic carbon and Acid Volatile Sulfide (AVS) concentrations that may occur in the site's sediments which may result in a higher RG.

The Environ RG for lead using the mummichog was based on a critical body burden (CBB) of 4 mg/kg lead, wet weight. The CBB method assumes that measured body burdens provide a good indicator of toxicity in the tissue where toxicity is exerted. The CBB, in this case, relies on the assumption that whole body concentrations represent good predictors of internal exposure and, thus, actual toxicity. The CBB seems to work well with hydrophobic substances. However, the application of the CBB to metals is not well established (EPA SAB 2005). Nonetheless, use of the CBB method for RG development was retained in GHD's analysis below of Environ's lead RG.

3. Biota to Sediment Accumulation Factor

3.1 Environ BSAF

The Environ RG for lead was developed from the CBB by extrapolation to a sediment concentration with a Biota to Sediment Accumulation Factor (BSAF). The BSAF estimates the concentration in fish based on the concentration in sediments.

$$BSAF = \frac{Pb_{fish}}{Pb_{sediments}}$$

Rearranging to solve for RG in sediments

$$RG_{sediments} = \frac{Pb_{fish}}{BSAF}$$

As shown in the equation, the RG is an inverse function of the BSAF. The Environ BSAF value is very conservatively¹ estimated from empirical data, from very different environments and very different fish (from Meador et al. 2005). The BSAF used by Environ was based on the average of BSAFs, 0.11 (unitless), from

¹ Because the RG decreases as BSAF increases, "conservative" here means BSAFs that are higher than best estimates.



several Pacific Ocean Bays, which had sediment lead concentrations about 1/15th of those that occur in Middle Creek. The resulting BSAF calculation includes a miscalculation and several conservative elements.

1. Environ estimated the whole body concentration of lead in fish as the simple average of the lead concentrations reported in three “tissues” from Table 3 of Meador et al.: muscle, liver, and “stomach”. Unfortunately, although the table refers to these concentrations as “tissue concentrations”, a closer reading of Meador et al. shows that “stomach” is not stomach tissue but rather “stomach contents.”² Moreover, since stomach contents contain large amounts of sediments, these concentrations tended to be much higher concentrations than actual fish tissues. Stomach contents are not relevant to the CBB method. Eliminating these data, and again, taking a simple average of the actual fish tissues shows much lower lead concentrations and a much lower average BSAF of 0.03, compared to 0.11. Because the RG varies inversely with the BSAF, this miscalculation significantly underestimates the RG.
2. The Environ BSAF includes several conservative assumptions. The BSAFs for metals and lead specifically are typically non-linear and inverse functions of ambient concentrations. The Meador et al. analyses demonstrate this log-log relationship between lead concentrations in sediments and fish livers. In addition, the bioaccumulation rate for metals and lead specifically declines with ambient concentrations. Therefore, application of BSAFs from low lead environments to high lead environments entails significant safety factors resulting in overly conservative criteria for protectiveness.
3. Given that BSAFs are log-log functions, a geomean BSAF is a more defensible statistic of likely conditions than the average BSAF. This is especially true at elevated lead concentrations. If a BSAF is calculated based on 1 and 2 above, the resulting much lower BSAF would produce a more representative, and much higher, RB.

In addition, the Meador et al. results are from low carbon environments (average of 0.89%), whereas Middle Creek is moderately carbon-rich, average of 3.1%. Data from Meador et al. and others (De Jonge et al. 2009) indicate that fish bioaccumulation of lead will be less in sediments with high binding capacity due to organic carbon, iron, or, potentially AVS.

3.2 BSAF Based on Iron Sequestration in Mid-Atlantic Estuary Environments

Due to the items identified above relating to Environ’s BSAF calculation, alternate BSAF estimates were sought for use in AOI -7 Ecological Risk Assessment based on data available since Environ generated the RG for lead. Recent analyses conducted for USEPA for the Passaic River (Louis Berger, 2014), which were not available when Environ calculated their RG for lead, effectively address all of the issues cited above. First, the underlying data are from a very similar and nearby ecological system and, they specifically pertain to the target fish species, mummichog. Thus, these predictions are species specific and more closely Site-specific. The range of underlying lead sediment concentrations is much closer to those of Middle Creek: an

² The text of Meador et al. is confusing as the terms “stomach” and “stomach contents” are used interchangeably in the document and the Table specifically refers to “tissue”. There is also no discussion in the Methods section about dissection of various tissues or how stomach contents were retrieved. However, a close reading of the discussion and the abstract make it clear that stomach refers to “stomach contents” and not the actual stomachs of the fish.



average of about 90 mg/kg in the lower Passaic compared to about 400 mg/kg in Middle Creek. The resulting predictive equations are based on the more biologically plausible log-log relationship and account for the potential binding capacity of sediments. Lastly, the methods have been externally reviewed and approved valid by USEPA for ecological risk assessment.

According to the methods (Louis Berger, 2014), wet weight lead concentrations in mummichogs, C_{fish} , can be estimated as

$$C_{fish} = e^{(B_0 + B_1 \ln(\frac{Pb}{f_{iron}}))}$$

Where B_0 and B_1 are regression coefficients, Pb is the sediment concentration of lead, and f_{iron} is the fraction of iron in the sediments. For mummichogs, B_0 and B_1 were estimated to be -7.125 and 0.755 respectively.

4. Calculated RG for Lead in Sediment of Middle Creek and Delaware River

The average iron concentration for sediments in Middle Creek is 59,000 mg/kg, or 5.9%. Applying this equation at the average iron concentration for Middle Creek produces a RG for the protection of fish of about 4800 mg/kg lead. Applying this equation to observed concentrations of lead and iron in specific samples of Middle Creek sediments estimates average mummichog concentrations of about 0.5 mg/kg wet weight lead concentrations well below the CBB of 4 mg/kg lead used in the Environ RG development.

Thus, this more robust BSAF predicts that lead concentrations in Middle Creek are almost an order of magnitude below levels that would cause any toxicity to mummichogs. It should also be noted that mummichogs were the most exposed to sediment lead of Passaic River biota. Estimated lead levels in eels, blue crab, and white perch were, respectively, about 2, 4, and 90 times lower than those estimated in mummichogs. Thus, the nearly Site-specific data and BSAF predictions from the Passaic River dismiss concerns about sediment lead toxicity to fish, mooted the need for any clean-up level protective of fish.

This same approach is applicable to calculating a lead RG for fish in the Delaware River since it also would be based on mummichogs. Using an observed iron concentration of 3%, the resulting clean-up level for lead based on fish in the Delaware River is about 2400 mg/kg.

Based on the analysis above, the appropriate RG for lead for the protection of fish would be 4800 mg/kg in Middle Creek and 2400 mg/kg in the Delaware River. Since the RG for the protection of fish is no longer the lowest value driving the RG, GHD evaluated the next value that would drive the RG, the protection of benthos. Environ proposed a RG of 570 mg/kg for the protection of benthos. GHD found this RG to be appropriate, unless it is superseded by site specific Acid Volatile Sulfide/ Simultaneously Extracted Metals (AVS/SEM) results which may result in a higher RG value based on site specific sampling data.



5. Conclusions

GHD reviewed the RG for lead in sediments produced by Environ. The most restrictive RG was 150 mg/kg protective of lead toxicity to mummichogs. The RG was based on a CBB of 4 mg/kg wet weight lead concentrations in mummichogs. The sediment concentration corresponding to this CBB was estimated with a BSAF, based on literature data on co-occurring concentrations of lead in fish tissue and sediments. The final sediment RG was estimated to be 150 mg/kg lead. However, the Environ BSAF is problematic in several respects. First, Environ's source document was unclear in its language. Consequently, Environ used data for "stomach contents" as stomach tissue data. In addition, use of the average BSAF assumes that the bioaccumulation relationship is linear. In fact, the BSAF is a declining function of sediment concentrations. Moreover, the data used in BSAF calculation were from much different environments and much different species than those in Middle Creek, and the calculations did not account for binding factors in the sediments that would affect bioaccumulation.

More recent analyses from USEPA's risk assessment for the Passaic River were identified that effectively addressed all of the issues identified above. First, the BSAF calculation methods were from a similar, and nearby environment in terms of both lead and sediment binding factors. Second, this BSAF prediction method specifically pertained to mummichogs, accounted for the binding capacity of the sediments, and was based on a log-log function. Third, the method has been found acceptable by USEPA for risk assessment.

Application of this more current BSAF method to Middle Creek estimated that sediment concentrations of 4800 mg/kg, and of 2400 mg/kg in the Delaware River, would be protective of fish. Since the RG for the protection of fish is no longer the lowest value driving the RG, GHD then evaluated the next value that would drive the RG, the protection of benthos. Environ proposed a RG of 570 mg/kg for the protection of benthos. GHD found this RG to be appropriate, unless it is superseded by site specific AVS/SEM results which may result in a higher RG value based on site specific sampling data.

6. References

- De Jonge, M. F. Dreesen, J. De Paepe, R. Blust and L. Bervoets. 2009. Do Acid Volatile Sulfides (AVS) Influence the Accumulation of Sediment-Bound Metals to Benthic Invertebrates under Natural Field Conditions? *Environ. Sci. Technol.*, 2009, 43 (12), pp 4510–4516.
- Environ. 2012. Evaluation of Sediment Remediation Goals For Former Industrial Facilities Claymont, Delaware. Prepared for Honeywell International Inc. and General Chemical, LLC, Claymont, Delaware. June 2012.
- Louis Berger. 2014. Lower eight miles of the Lower Passaic River: data evaluation report no. 6: Biota Analysis. Report prepared for USEPA by the Louis Berger Group, Inc., in conjunction with Battelle.
- Meador, J.P., D.W. Ernest, and A.N. Kagley. 2005. A Comparison of the Non-essential Elements Cadmium, Mercury, and Lead Found in Fish and Sediment from Alaska and California. *Sci. Total Environ.* 339:189:205.